II.G High-Temperature Thermochemical Processes

II.G.1 High Efficiency Generation of Hydrogen Using Solar Thermochemical Splitting of Water*

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The National Renewable Energy Laboratory, Golden, CO

**Congressionally directed project*

Objectives

- Identify and demonstrate high-efficiency, competitive-cost solar-powered thermochemical concepts for the production of hydrogen from water
- Establish feasibility of promising concepts using data from laboratory experiments

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- C. Feedstock and Water Issues
- D. Carbon Dioxide Emissions
- F. Feedstock Cost and Availability
- J. Rate of Hydrogen Production
- Q. Cost
- T. Renewable Integration
- V. High- and Ultra-High-Temperature Thermochemical Technology
- W. High Temperature Materials
- X. Policy and Public Acceptance
- Y. Solar Capital Cost
- AC. High-Purity Water Availability

Approach

- Design and implement a quantitative comparative assessment methodology to screen all known thermochemical cycles and select the top several performers
  - Perform qualitative comparative assessment of the approximately 200 known thermochemical water-splitting cycles, winnowing to about 20-25 candidates
  - Identify quantitative thermochemical performance data relevant to cycle efficiency and cost in existing literature
  - Design solar receiver, chemical reactor concepts appropriate to cycle chemistry and solar collector technology
  - Perform second level comparative assessment to identify ~3 competitive concepts
  - Demonstrate and test appropriate receiver/reactor designs as necessary
  - Acquire missing or uncertain quantitative thermodynamic data and develop detailed process flow sheets for receiver/reactor designs integrated with the thermochemical process
  - Quantify cost and efficiency of 3 best concepts integrated with appropriate solar collector technologies
  - Define pilot/demonstration plant concept
- Perform literature surveys and laboratory experiments to acquire essential evaluation and design data for the top several concepts
- Perform kinetics studies on ZnO reduction process
  - Design ZnO reduction kinetics experimental campaign using variable residence time of ZnO feedstock in the reactor hot zone and variable quench rate of zinc and oxygen vapors
  - Prepare for kinetics experiments on Mn_2O_3 reduction
- Design (and test/demonstrate where appropriate) collector/receiver/reactor components for integrated system analysis
- Analyze cost and efficiency metrics for integrated cycle performance
- Develop demonstration/pilot plant concept designs for surviving competitive cycles
- Provide recommended path forward

Accomplishments

- Documented 74 thermochemical cycles previously not screened for performance for a (current) total of ~196 known thermochemical cycles
- Developed web-based database management and automated scoring system for comparative assessment of thermochemical cycles
- Scored the first 122 thermochemical cycles and initiated engineering analysis for Phase 2 screening of a number of these cycles (final number to be determined by complete Phase 1 screening)
- Demonstrated better than 50% zinc metal recovery from reduction of ZnO at approximately 1700 C
- Designed a water-cooled injection “lance” for control of feedstock residence time
- Designed a water-cooled quench probe for quench rate control of zinc and oxygen vapors
- Testing of a conceptual ZnO particle feed apparatus is underway

Future Directions

- Develop block diagrams of remaining 74 thermochemical cycles and complete Phase 1 screening
- Perform engineering analysis and develop process flow sheets for the top 20-25 Phase 1 survivors that are assessed to be thermodynamically feasible

- Complete Phase 2 screening to identify the top ~3 surviving cycles
- Measure performance of a porous-wall aerosol reactor for design of a fluid-wall reactor for isolation of graphite reactor walls from reactants and aerosol
- Design, fabricate and test an improved particle feed device for flowing aerosol reactor
- Perform quantitative kinetics experiments on ZnO reduction with
  - A water-cooled insertion “lance” for measurement of residence-time effects on ZnO reduction
  - A water-cooled quench tube to observe effects of quench rates on metallic zinc recovery
- Initiate design and implement model/simulation analysis of top cycles integrated with collector/receiver/ reactor designs
- Develop quantitative cost and efficiency metrics for these top cycles
- Proceed to demonstration/pilot plant design with a positive decision

Introduction

Solar-powered thermochemical water splitting produces hydrogen using only water, heat from the sun, and chemicals that are completely re-cycled so that only hydrogen and oxygen are produced and only water is consumed in the cycle. Thermochemical water splitting has been shown feasible in a number of different studies [Refs. 1, 2, 3, 4, 5]. All known thermochemical cycles face obstacles that could include extremely high temperature, highly corrosive chemicals, difficult separations of chemicals during sequential cycle steps, multiple reaction steps necessary to close the cycle, or side reactions with stable products that poison the process upon recycling. Many of these barriers can be overcome, but generally at the expense of energy efficiency, consumption of feedstocks other than water, or even higher temperature to drive reactions to completion. All of these measures add cost to the product, inhibit acceptable production rates, or prevent the realization of plant designs with acceptable lifetimes. Overcoming these barriers is even more difficult if solar radiation is to be used as the process energy, primarily because of its transient nature and diffuseness[6, 7]. Transient operation is not an option for most chemical plants because of the enormous difficulty of starting and achieving stable operations, particularly for large plants. At the same time, solar energy requires large collector areas and efficient concentrators to power energy-intensive processes.

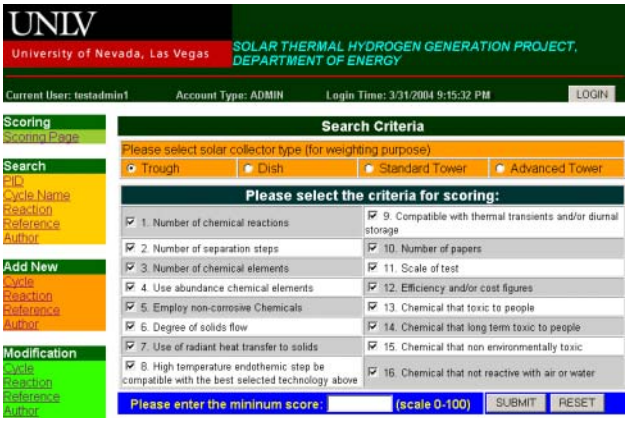
Advances in solar collector materials and designs, development of advanced corrosion-resistant materials, the discovery of new membrane technology for efficient separations, and the likelihood that at least some cycles will be adaptable to transient operations has stimulated the current project to identify a few promising cycles, to develop operational plant designs, and to establish cost and profitability metrics.

Approach

Qualitative comparative assessment of the nearly 200 water splitting cycles referenced in the literature is used to reduce the number of likely candidates for more quantitative evaluation. This process is not to identify winners but to identify cycles unworthy of further assessment. This qualitative assessment is based on objective block diagrams of each process to identify the number of reaction steps and reaction temperatures, the physical state of the reactants and products (solid, liquid, vapor), the number of separations, and conceptual description of connections of one step to the next. Sixteen criteria that affect cost, development risk, environmental risk, and sensitivity to power transients are identified using expert judgment. Simultaneously, fundamental performance metrics for promising cycles (e.g.,metal oxide cycles) are being established with laboratory experiments so that these processes may be considered. All cycles are automatically scored against four solar collector options (trough, standard tower, dish and advanced tower) using software developed for this purpose and for project data management. About 20-25 of the survivors of this qualitative assessment will be subjected to detailed engineering evaluation that addresses cycle thermodynamics, estimated performance of solar collector/receiver options, and development of process flow sheets to permit estimates of process efficiency, the primary Phase 2 screen. The ~3 apparently best cycles will be developed in detail through component design, integrated plant conceptual design, integrated process flow sheet development, and process and component simulation to permit quantitative cost and efficiency analysis. Demonstration/pilot plant designs will be initiated and recommendations for further work will be provided for concepts that remain competitive according to Hydrogen Program Plan metrics.

Results

Figure 1 shows the main automated scoring page of the database management and automated scoring software developed during the first half year. 122 of the ~ 196 thermochemical cycles were screened according to criteria and weighting factors shown in Figure 2. The remaining 74 cycles are in process of block diagram development and database updates.



SOLAR THERMAL HYDROGEN GENERATION PROJECT, DEPARTMENT OF ENERGY

Current User: testadmin1 Account Type: ADMIN Login Time: 3/31/2004 9:15:32 PM

Search Criteria

Please select solar collector type (for weighting purpose)

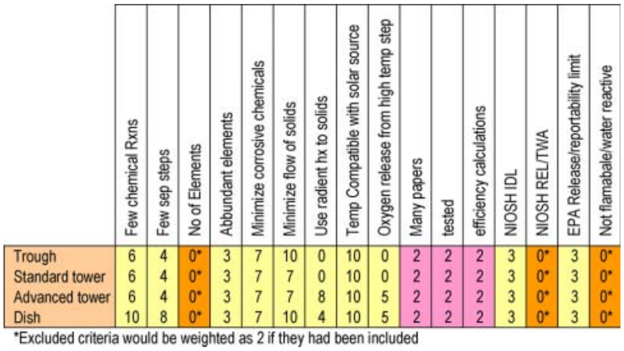
● Trough ○ Dish ○ Standard Tower ○ Advanced Tower

Please select the criteria for scoring:

☑ 1. Number of chemical reactions	☑ 9. Compatible with thermal transients and/or diurnal storage
☑ 2. Number of separation steps	☑ 10. Number of papers
☑ 3. Number of chemical elements	☑ 11. Scale of test
☑ 4. Use abundance chemical elements	☑ 12. Efficiency and/or cost figures
☑ 5. Employ non-corrosive Chemicals	☑ 13. Chemical that toxic to people
☑ 6. Degree of solids flow	☑ 14. Chemical that long term toxic to people
☑ 7. Use of radiant heat transfer to solids	☑ 15. Chemical that non environmentally toxic
☑ 8. High temperature endothemic step be compatible with the best selected technology above	☑ 16. Chemical that not reactive with air or water

Please enter the mininum score: (scale 0-100)

Figure 1. Main Automated Scoring Page



	Few chemical Rxns	Few sep steps	No of Elements	Abbundant elements	Minimize corrosive chemicals	Minimize flow of solids	Use radient hx to solids	Temp Compatible with solar source	Oxygen release from high temp step	Many papers	tested	efficiency calculations	NIOSH IDL	NIOSH REL/TWA	EPA Release/reportability limit	Not flamabale/water reactive
Trough	6	4	0*	3	7	10	0	10	0	2	2	2	3	0*	3	0*
Standard tower	6	4	0*	3	7	7	0	10	0	2	2	2	3	0*	3	0*
Advanced tower	6	4	0*	3	7	7	8	10	5	2	2	2	3	0*	3	0*
Dish	10	8	0*	3	7	10	4	10	5	2	2	2	3	0*	3	0*

*Excluded criteria would be weighted as 2 if they had been included

Figure 2. Weighting Factors for the Various Collector Concepts

The result of Phase 1 screening of the first 122 cycles for an advanced power tower option is shown in Figure 3. Similar results have been developed for screening of the first 122 cycles against the trough, the standard tower and the dish options. Figure 4 shows an example of a study of screening sensitivity to all weighting factors simultaneously. If the top 30 cycles are selected (corresponding to a normalized score of 40), three unweighted cycles would score less than 40 and no cycles with weighted scores of less than 40 would score higher than 40. No cycles among the top 30 are excluded because of weighting. If the top 25 cycles are selected (corresponding to a normalized score of 44), four unweighted cycles would score less than 44 and one unweighted score would be higher than 44. One cycle is excluded from

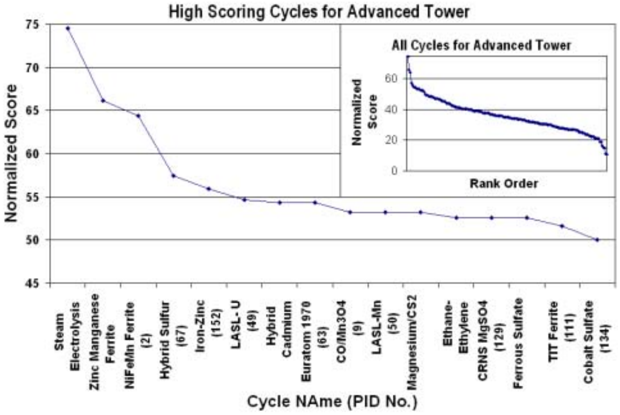


Figure 3. Advanced Power Tower Screening Result for the Initial 122 Cycles

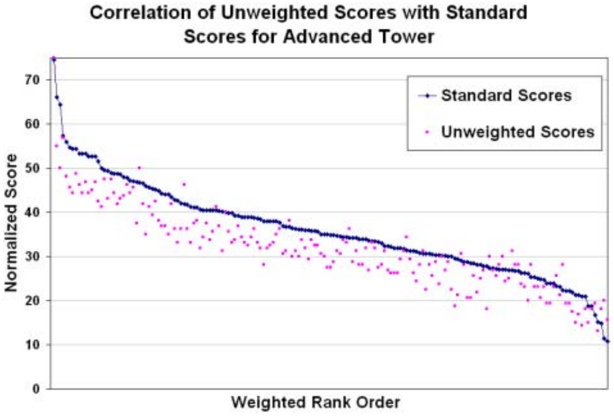


Figure 4. Example of Scoring Sensitivity to Weighting Factors

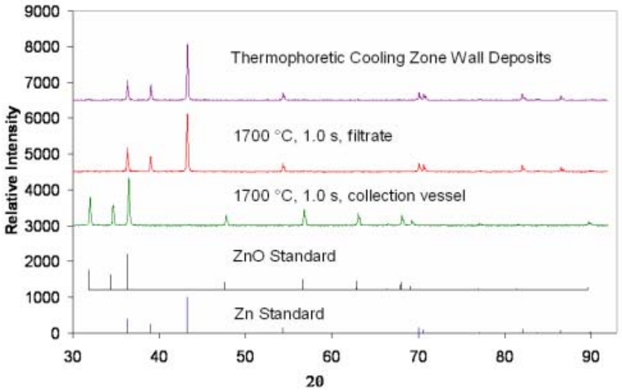


Figure 5. Evidence of Zn Metal Recovery from ZnO Reduction

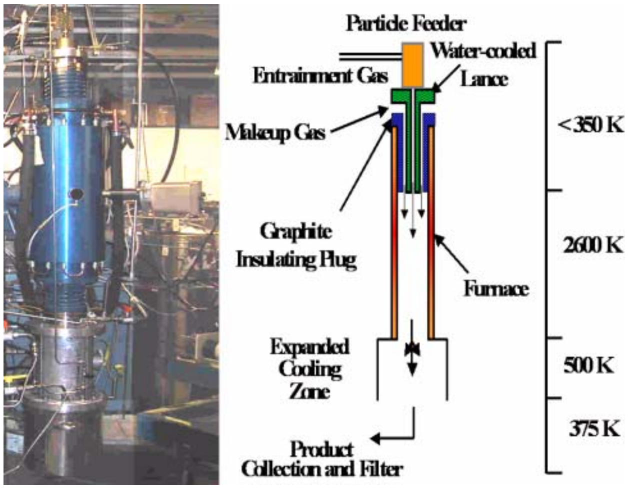


Figure 6. Flowing Aerosol Reaction Apparatus with Improved Injector Design

the top 25 because of weighting factors. As is frequently the case with qualitative numerical scoring of comparable entities, particular attention must be paid to marginal events. Cycles that exhibit sensitivity to weighting will be scrutinized to guard against unwarranted elimination of any cycle.

Figure 5 shows X-ray spectral evidence of recovery of metallic zinc from reduction of ZnO at 1700 C. Analysis of experiments confirms that more than 50% of ZnO is converted to Zn and oxygen gas when an inert carrier gas is implemented. These promising results stimulated the design of a porous wall aerosol flow reactor with a water-cooled injection lance shown in Figure 6 that will control residence time (by streamwise location of the injection lance relative to the quench zone), protect the graphite reactor walls from oxidation, and prevent deposition of reactants and products on the reactor walls. Experiments are underway to establish reactant residence time effects in the reactor to assist in the final design and fabrication of this improved reactor. Quench rate experiments using a water-cooled quench tube inserted downstream from the reaction zone are also in development.

Conclusions

Assumption-driven assessments of thermochemical hydrogen production by the sulfur-iodine cycle and the zinc oxide cycle were found to indicate that a solar-powered water-splitting hydrogen production concept could be competitive with other processes, at least for some reasonable scenarios. Phase 1 screening appears to be sufficiently insensitive to subjective weighting factors to warrant this approach to reducing the inventory of thermochemical cycles for detailed analysis. Phase 2 screening is underway to identify the few remaining cycles for highly detailed quantitative evaluation.

Reduction of ~50% particulate ZnO feedstock to metallic Zn has demonstrated the feasibility of this process, warranting continued development of performance metrics and reaction kinetics to permit competition of this cycle, which can be operated in a mode that is insensitive to power fluctuations. Advanced reactor design concepts for quantitative Zn cycle experiments are in development through experiments designed to identify residence time effects, quench rate effects, and performance of a porous graphite wall design to prevent contamination of the reactor wall.

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